

Short communication

Starch/rosin complexes for improving the interaction of mineral filler particles with cellulosic fibers

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ABSTRACT

On the basis of inclusion complex formation of starch with small guest molecules, the concept of filler modification for papermaking by calcium-ion-induced deposition of starch/rosin complexes in the presence of filler particles was demonstrated. The rosin amount of 3% (on the basis of the dry weight of starch) induced effective starch deposition. Due to the cellulose-bondable nature of starch/rosin complexes, filler modification resulted in improved interaction of precipitated calcium carbonate particles with cellulosic fibers, leading to reduced negative impact of filler addition on paper strength. The efficiency of alkyl ketene dimer emulsion as an internal sizing agent for cellulosic paper was also improved as a result of filler modification. The concept demonstrated in this study may provide a useful alternative to the improvement of the use of mineral fillers in the paper industry.

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1. Introduction

As a biopolymer, starch can form inclusion complexes with small molecules (Byars, Fanta, & Kenar, 2013; Heinemann, Escher, & Conde-Petit, 2003; Kenar, Eller, Felker, Jackson, & Fanta, 2014). In this regard, small guest molecules are constrained in the structure of starch, leading to the encapsulation of the guest molecules with starch based on host–guest interactions.

Since starch is chemically similar to cellulosic fibers, encapsulation of filler particles for papermaking applications with starch can improve their bondabilities with cellulosic fibers, allowing for increasing the filler content of paper products while maintaining their critical properties (Yan, Liu, & Deng, 2005; Zhao, Hu, Ragauskas, & Deng, 2005). This increase in filler content can provide cost/energy savings associated with the use of mineral fillers less costly than cellulosic fibers (Deng, Jones, McLain, & Ragauskas, 2010). Interestingly, the combination of starch with a fatty acid can induce the effective deposition of cooked starch on filler particles in an aqueous medium, due to the decrease in water-solubility (and also the increase in hydrophobicity) of starch as a result of the inclusion of fatty acid molecules more hydrophobic than starch (Cao, Song, Deng, & Ragauskas, 2011; Deng et al., 2010; Huang, Shen, & Qian, 2013; Yoon & Deng, 2006).

In the current study, the filler modification process concept involving the calcium-ion-induced deposition of starch/rosin complexes in the presence of filler particles was demonstrated. It was hypothesized that such a process concept may provide an alternative to filler bondability improvement. Since rosin-based sizing agents are traditionally used in the paper industry to deliver enhanced hydrophobicity, filler modification with starch/rosin complexes is also likely to enhance the efficiency of internal sizing agents.

2. Materials and methods

2.1. Materials

Powdered corn starch without any chemical treatment was supplied by Shandong Runyin Biochemical Engineering Co., Ltd., China. Rosin was provided by Jinan Changyingda Chemicals Co., Ltd., China. Precipitated calcium carbonate filler with an ISO brightness of 92.4% was sourced from Guangxi Guilin Wuhuan Co., Ltd., China. Softwood-derived bleached chemical pulp (cellulosic fibers) was obtained from Mudanjiang Hengfeng Paper Co. Ltd., China. This pulp was refined to 31°SR using a Valley refiner. Alkyl ketene dimer emulsion was supplied by Mudanjiang Hengfeng Paper Co. Ltd., China. Cationic polyacrylamide (Percol® 182) and bentonite (Hydrocol® AP1), commonly used as a microparticle retention system for cellulosic paper stock, were provided by BASF (China).

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Co., Ltd. Sodium hydroxide and calcium chloride were analytical reagents.

2.2. Filler modification by deposition of starch/rosin complexes in the presence of filler particles

To a 250 ml flask, 3 g of starch (on a dry weight basis) was added. Distilled water was added, and the total weight of the mixture was adjusted to 100 g. The mixture was stirred and heated to 95 °C, followed by cooking at this temperature for 1 h. Rosin soap solution (prepared by the reaction of rosin with sodium hydroxide) was added, and the mixture was re-heated to 95 °C and cooked at this temperature for 30 min. The resulting mixture was then cooled down and diluted to 500 ml.

To a 200 ml of 0.2 mol/l calcium chloride solution, 6 g of precipitated calcium carbonate filler was added and sufficiently mixed. Upon heating to 90 °C, 200 ml of the as-prepared mixture containing starch/rosin complexes was added, followed by mixing for 30 min. The mixture was then sufficiently washed by centrifugation to remove the excess calcium ions. It should be noted that the resulting slurry was allowed to stand for 24 h prior to macroscopic optical image observations and turbidity measurement (WGZ-200 turbidity tester (China) with a measuring range of 0 to 200 NTU).

2.3. Paper-sheet preparation and determination of paper properties, filler retention and filler bondability factor

Cellulosic fibers and filler (fibers/filler weight ratio: 4:1, on a dry weight basis) were sufficiently mixed, followed by the sequential addition of alkyl ketene dimer emulsion, cationic polyacrylamide solution, and bentonite slurry. The resulting furnish was made into

paper-sheets with a target grammage of 60 g/m² by using a ZQJ1-B200 mm sheet former (China). The wet paper-sheets were pressed at 0.4 MPa for 5 min prior to drying (105 °C, 5 min). It should be noted that the dosages of alkyl ketene dimer emulsion, cationic polyacrylamide, and bentonite were 0.11%, 0.05%, and 0.5%, respectively, based on the total dry weight of cellulosic fibers and filler.

After drying, the paper-sheets were conditioned sufficiently in a glass desiccator, and tensile strength was tested by using a ZL-300A tester (China) (Huang, Sun, Qian, Li, & Shen, 2014a). Paper brightness and opacity were determined by using a YQ-Z-48A tester (China). To evaluate the impact of filler modification on sizing, the Stockigt sizing degree of the paper-sheets was tested. Filler retention was determined by following the procedures reported by Shen, Song, Qian, and Yang (2010). Filler bondability factor was calculated based on the following equation (Huang, Sun, Qian, Li, & Shen, 2014a,b):

$$\text{filler bondability factor} = \frac{\text{strength of filled paper}}{\text{strength of unfilled paper}} \times \text{filler content of filled paper} \times 100$$

2.4. SEM observations

SEM observations of filler particles and paper-sheets were conducted using a scanning electron microscope (SEM, QUANTA 200).

3. Results and discussion

Chemically, starch is a mixture of amylose and amylopectin, both of which can form inclusion complexes with certain small

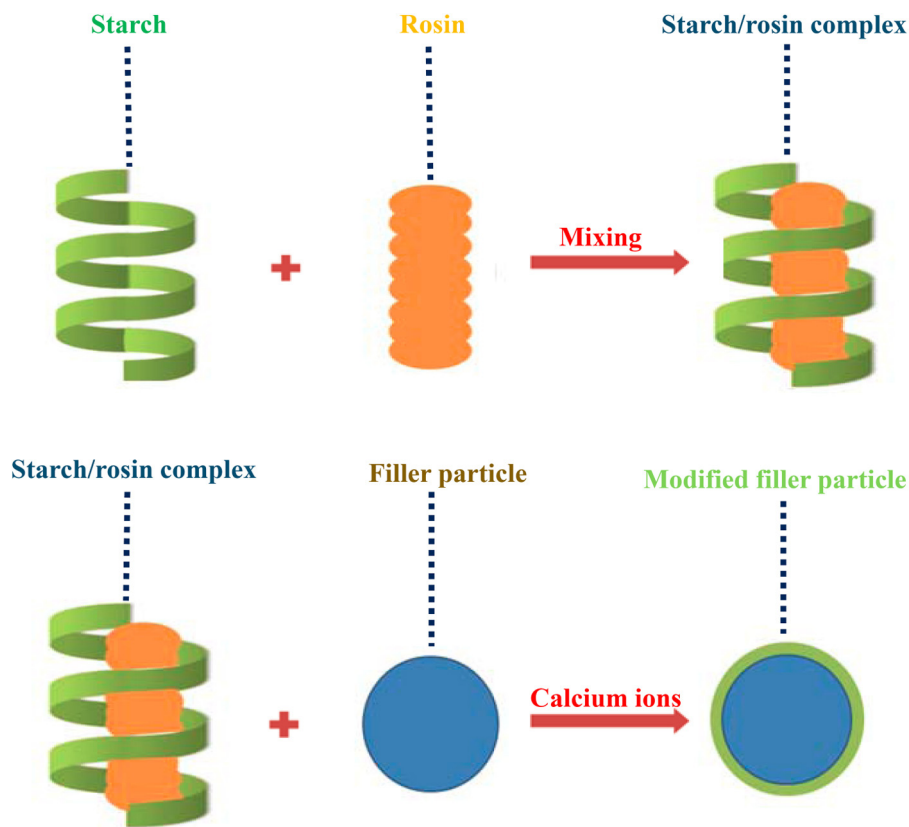


Fig. 1. Schematic illustration of the formation of a starch/rosin complex and its deposition on filler with the aid of calcium ions. Note that the shapes of filler, rosin, and starch as well as the interactions between starch and rosin are for illustration purpose only, and they are not representative of the real shapes of molecules and the concretely defined intermolecular interactions.

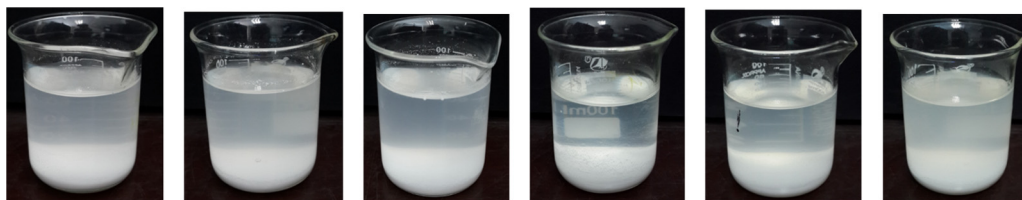


Fig. 2. Macroscopic optical photographs of modified-filler-containing aqueous mixtures. Note: (a) From left to right, the amounts of rosin during filler modification process were 0, 1%, 2%, 3%, 5%, 7%, 10%, respectively, based on the dry weight of starch; (b) the freshly prepared aqueous mixtures were allowed to stand for 24 h prior to observations.

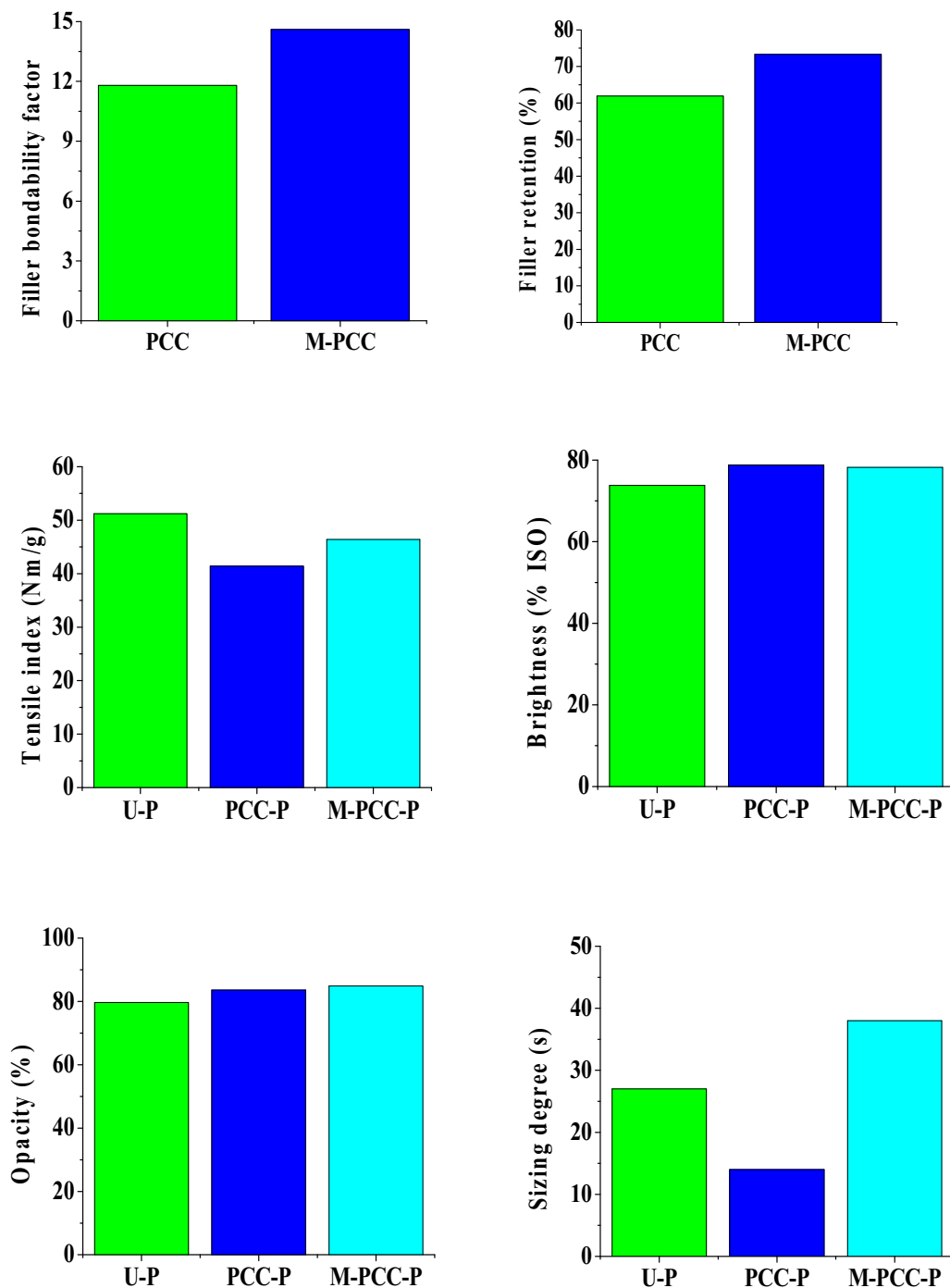


Fig. 3. Impact of filler modification on tensile index, brightness, opacity, and Stockigt sizing degree of paper-sheets as well as filler bondability factor and filler retention. Note: PCC and M-PCC refer to unmodified precipitated calcium carbonate filler and modified precipitated calcium carbonate, respectively; UP, PCC-P, and M-PCC-P refer to unfilled paper, unmodified-filler-filled paper, and modified-filler-filled paper, respectively.

guest molecules (Kasemwong & Itthisoponkul, 2013). The characteristics of starch can be tailored by inclusion complex formation. On the basis of these fundamentals, filler modification for paper-making by encapsulation of filler particles with starch/fatty acid inclusion complexes has been an interesting topic (Cao et al., 2011; Deng et al., 2010; Huang et al., 2013; Yoon & Deng, 2006).

Differing from previous reports, the concept of filler modification by calcium-ion-induced-deposition of starch/rosin complexes in the presence of filler particles was proposed, which is schematically illustrated in Fig. 1. Two main elements are involved in the filler modification process: (1) formation of starch/rosin complexes under sufficient mixing of dissolved starch with dissolved rosin in an aqueous medium, and (2) calcium-ion-induced deposition of starch/rosin complexes in the presence of filler particles.

Once starch is sufficiently cooked/gelatinized, it can be dissolved in water. Under mixing, rosin molecules (guest molecules) dissolved in water can enter the cavities of dissolved starch (host molecules) (Deng, Yoon, Ragauskas, & White, 2011), which is in some sense similar to cellulosic fiber lumen loading with mineral particles. However, for the effective deposition of starch/rosin complexes in the presence of filler particles, either acidification or calcium ion treatment (Cao et al., 2011; Deng et al., 2010; Huang

et al., 2013; Yoon & Deng, 2006) is desired to decrease the solubility of the complexes via the interaction of acids or calcium ion with rosin soap in the complexes. In this study, calcium-ion-induced precipitation (Huang et al., 2013) was adopted, which is expected to be applicable to acid-unstable calcium carbonate fillers or other types of mineral fillers.

Based on optical photographical observations and turbidity analysis (Huang et al., 2013), a rosin amount of 3% (based on the dry weight of starch) was effective in inducing starch precipitation; however, a lower or higher amount was less favorable for starch precipitation (see Fig. 2 and Table 1). It should be noted that different from the linear structure of fatty acids, rosin is a mixture of different molecules, mainly characterized by three consolidated six-carbon rings, double bonds that differ in number and location, and a carboxylic acid group. Thus, the interaction of starch with fatty acids would be different from that with rosin. It was found that under the conditions of filler modification reported by Huang et al. (2013), efficient formation/deposition of starch/rosin complexes was not initiated; however, the filler modification process in this work (see Section 2) resulted in effective starch deposition based on starch/rosin complex formation and calcium ion treatment. It is likely that the filler modification process involving the mixing

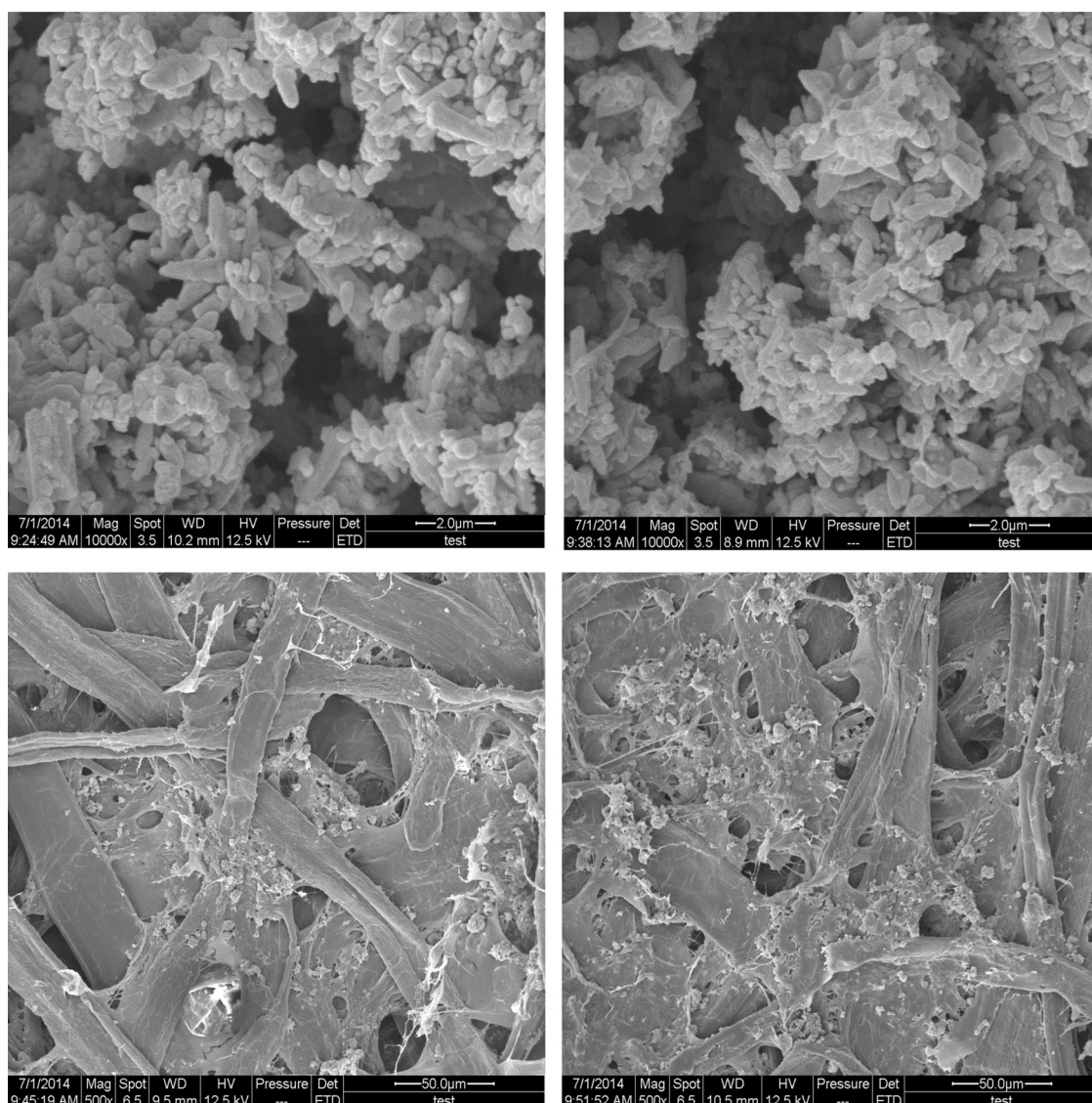


Fig. 4. SEM images of unmodified filler (top, left), modified filler (top, right), unmodified-filler-filled paper (bottom, left), and modified-filler-filled paper (bottom, right).

Table 1
Turbidities of the supernatants of modified-filler-containing aqueous mixtures.

Amount of rosin during filler modification process (%)	Turbidity (NTU)
0	BMR
1	BMR
2	125.3
3	27.4
5	73.3
7	BMR

Note: The turbidities were measured after allowing the aqueous mixtures to stand for 24 h; BMR refers to “beyond measuring range”.

of starch/rosin/filler/calcium ion-based composition at a high temperature (90 °C) facilitated the swelling of starch molecules, leading to enlarged cavities favorable for inclusion of rosin molecules in the structure of starch.

As shown in Fig. 3, filler modification resulted in a simultaneous significant increase in filler retention and the tensile strength of the paper, and hence a pronounced increase in filler bondability factor (from 11.8 to 14.6). This indicated that the negative impact of filler addition on paper strength was reduced due to the cellulose-bondable nature of starch/rosin inclusion complexes. The surface encapsulation of filler with starch/rosin complexes and the increase in filler retention as a result of filler modification may also be seen from Fig. 4. On the other hand, the influence of filler modification on paper brightness/opacity was basically negligible (see Fig. 3). Interestingly, filler modification resulted in an increase in the Stockigt sizing degree of the paper (see Fig. 3); in other words, paper hydrophobicity was improved as a result of filler modification. This is due to the hydrophobic nature of rosin, the emulsion/dispersion of which is traditionally used as an internal sizing agent in the paper industry. However, the use of unmodified mineral fillers in the paper industry is known to have a negative impact on the efficiency of sizing agents, due to the much higher specific surface area of filler particles in comparison to cellulosic fibers and hence the preferable adsorption of size particles on filler (Shen, Song, Qian, & Liu, 2009). Therefore, the interaction of filler particles with cellulosic fibers in terms of the impact of filler addition on paper strength and sizing efficiency was substantially improved as a result of filler modification.

4. Conclusions

Filler modification for papermaking by calcium-ion-induced deposition of starch/rosin complexes in the presence of filler particles was explored. In the presence of retention system consisting of cationic polyacrylamide and bentonite, filler modification resulted in an increase of filler bondability factor from 11.8 to 14.6. As a result of filler modification, filler retention was increased, while

paper brightness/opacity was not significantly influenced. The favorable impact of filler modification on the efficiency of alkyl ketene dimer as a sizing agent was also identified.

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